(2)

TECHNICAL REPORT
NATICK/TR-85/047

AD_____

DEGRADATION OF NITROGUANIDINE

AD-A157 859

BY
DAVID L. KAPLAN
ARTHUR M. KAPLAN

JANUARY 1985

FINAL REPORT 1984

DTIC
ELECTE
AUG 13 1985
S D

DTIC FILE COPY

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

UNITED STATES ARMY NATICK
RESEARCH AND DEVELOPMENT CENTER
NATICK, MASSACHUSETTS 01760-5000

SCIENCE & ADVANCED TECHNOLOGY LABORATORY

85 8 6 068

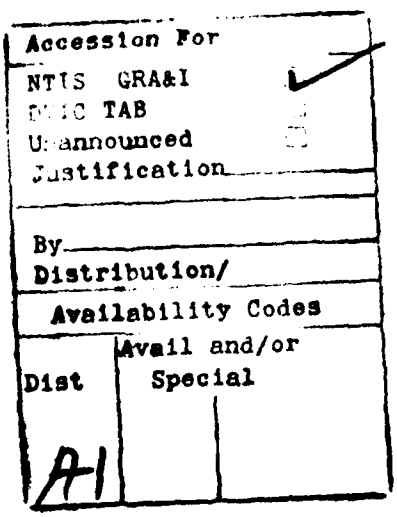
Disclaimers

The findings contained in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

DESTRUCTION NOTICE

For classified documents, follow the procedures in DoD 5200.1-R, Chapter IX or DoD 5220.22-M, "Industrial Security Manual," paragraph 19. For unclassified documents, destroy by any method which precludes reconstruction of the document.



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NATICK/TR-85/047	2. GOVT ACCESSION NO. AD-A157859 / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* DEGRADATION OF NITROGUANIDINE IN SOILS	5. TYPE OF REPORT & PERIOD COVERED Final Report, 1984 6. PERFORMING ORG. REPORT NUMBER NATICK/TR-85/047
7. AUTHOR(s) David L. Kaplan and Arthur M. Kaplan	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U. S. Army Natick R&D Center ATTN: STRNC-YEP Natick, MA 01760-5020	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6.1, PT12.03.0742 691000.H6800 1L161102AH68
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Toxic and Hazardous Materials Agency ATTN: AMXTH-TE-D Aberdeen Proving Ground, MD 21010	12. REPORT DATE January 1985 13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*	15. SECURITY CLASS. *(of this report)* UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

DEGRADATION	CONTAMINATION
NITROGUANIDINE	GUANIDINE NITRATES
SOILS	LAND APPLICATION
WASTEWATER	ENVIRONMENTS
CARBON	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The degradation of nitroguanidine in soil was studied with continuous flow soil columns. Nitroguanidine was biodegraded if sufficient supplemental carbon was provided in the wastewater. The primary product formed during the biodegradation of nitroguanidine in soil was ammonia. Only trace concentrations of nitrosoguanidine were detected and no significant levels of other organic-nitrogen compounds, nitrates or nitrites were present in column leachates.

(cont'd)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

These results indicate that land applied process water laden with nitroguanidine can be successfully treated on a short-term basis with minimal impact on soils and groundwater. It is imperative however, to provide sufficient supplemental carbon for this process, otherwise the nitroguanidine will not degrade and will leach directly into groundwaters.

Preliminary work with guanidine nitrate showed this compound to be biodegradable under anaerobic conditions, but this process will most likely also require supplemental carbon.

Recommendations for monitoring requirements with a land application system are provided as well as an alternative solution for long-term treatment of nitroguanidine manufacturing wasterwaters.

PREFACE

Recent one-time land application of prove-out wastewaters at Sunflower AAP, DeSoto, Kansas, prompted this investigation. It became necessary to understand the degradative mechanisms of nitroguanidine in soil in order to evaluate the environmental impact of this application. Land application, if feasible, does not pose a significant risk to health or environment, and would be a low cost solution to treatment of wastewater contaminated with nitroguanidine.

This work was performed for the US Army Toxic & Hazardous Materials Agency under project number 1L161102AH68, 691000.H6800 . This report covers work completed up to the premature termination of the program due to an administrative decision at Natick.

We wish to thank Dr. Joseph Akkara, Steven LaRosa, Jennifer Pierce and Silvino Sousa, all of the Science & Advanced Technology Laboratory of the US Army Natick R&D Center, for their technical assistance.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

DEGRADATION OF NITROGUANIDINE IN SOIL

INTRODUCTION

Land disposal was used to treat approximately 5 million gallons of prove-out wastewaters from nitroguanidine manufacture at Sunflower Army Ammunition Plant (AAP) DeSoto, Kansas, in 1983. The wastewater had been stored in concrete settling basins after prove-out runs of the plant. This material was spray irrigated over 150 acres of land at Sunflower AAP with state approval as a one-time solution. The concentrations of nitroguanidine and guanidine nitrate had decreased to below 0.2 mg/L and 0.1 mg/L, respectively, by the time the stored wastewaters were applied to the soil.[1] Exposure of the nitroguanidine in the settling basins to sunlight was the primary reason for the low residual concentration. The sensitivity of nitroguanidine to UV light has been previously reported.[2]

The environmental quality of the land application site was assessed by the US Army Environmental Hygiene Agency (AEHA) both before and after the application.[1] Since residual concentrations of nitroguanidine and guanidine nitrate were very low, it was difficult to address the environmental impact of these compounds. However, the effects of the nutrients contained in this wastewater, particularly nitrogen compounds, was addressed with regard to nutrient loadings.

The objective of this program was to evaluate the soil degradation mechanisms for nitroguanidine and determine the feasibility of land application as a low cost treatment option for these wastewaters. In addition, preliminary work was performed to evaluate the biodegradability of guanidine nitrate.

MATERIALS AND METHODS

Chemicals. Nitroguanidine was provided by Hercules, Inc., Sunflower AAP, DeSoto, Kansas, and was 99+% pure. Nitrosoguanidine was previously synthesized.[2] Cyanamide, cyanoguanidine, guanidine hydrochloride, and melamine were purchased from Eastman Kodak Co., Rochester, NY. Urea was purchased from Fisher Scientific Co., Medford, MA. Carbohydrazide was purchased from Fluka Chemical Co.

Soil Columns. Glass columns, 40 cm tall by 7 cm diameter, were filled with 1000 g dry weight of soil. The soil was garden soil, 6.4% organic matter and pH 6.9, and had been passed through a 2-mm sieve. The soil was retained in the columns with polyethylene screening, 202 μm pore size. The nitroguanidine solutions were continuously pumped (Rainin Rabbit peristaltic pump) through silicone tubing onto the tops of the columns. The feed solution leached through the soil via gravity. All active columns were inoculated. The organisms were from a mixture of activated sludge (Marlborough Easterly Sewage Treatment Plant, Marlborough, MA), anaerobic sludge digest (Nut Island Sewage Treatment Plant, Quincy, MA), and garden soil. The combined samples were diluted

with 0.085% potassium chloride, filtered, and the filtrate was used as the inoculum.

Nitroguanidine, 150 mg/L, was dissolved in tap water and the solution autoclaved. In the active column, after the initial period without glucose, the concentration of glucose was set at 2.0 g/L and decreased periodically during the study. Control columns were run with tap water, nitroguanidine in tap water without the glucose, and nitroguanidine in tap water with mercuric chloride (Table 1). Media flowed at around 100 mL/day.

TABLE 1. Experimental Conditions for Soil Columns.

No.	Microorganisms (sterile[a]/active)	Medium	Carbon Supplement
1	Active	Tap water	None
2	Active	Nitroguanidine	Variable[b](0 to 2g/L)
3	Sterile	Nitroguanidine	None
4	Active	Nitroguanidine	Glucose (0.75 g/L)
5	Active	Tap Water	Variable[c]
6	Sterile	Tap Water	Variable[c]

[a] 1.0% mercuric chloride

[b] glucose concentration, initiated at 0

[c] initial one-time load of columns

Sampling and Analysis. Twice weekly or weekly samples (influent and leachates) from the soil columns were evaluated for oxidation-reduction potential, pH, nitrites, nitrates, ammonia, total organic carbon (TOC), nitroguanidine, and nitrosoguanidine. In addition, solutions were concentrated 100-fold and evaluated by thin layer chromatography (TLC) for potential intermediates by previously described methods.

Oxidation-reduction potential was determined with a redox platinum electrode (Orion) and reported in relative millivolts. Hydrogen ion concentration was determined with a calomel electrode (Corning). Both pH and redox were monitored on a Corning model 130 pH meter. Ammonia was determined with a specific ion electrode (Orion). Low concentrations (<1 mg/L) of nitrite were determined by a standard colorimetric method using a Lambda 3 spectrophotometer (Perkin Elmer, Norwalk, CT). Higher concentrations of nitrites and nitrates were determined by high performance liquid chromatography (HPLC).

Total organic carbon was determined with a Beckman 915B Tocamaster with Matheson Ultra Zero Air as carrier gas flowing at 300 mL per minute. Samples, 200 µL, were delivered with a Hamilton CR-200 200 µL constant rate syringe.

High Performance Liquid Chromatography. Nitroguanidine and nitrosoguanidine were analyzed on a Water's (Water's Associates, Milford, MA) HPLC consisting of a M721 System Controller, M730 data module, M440 Absorption detector set at 254 nm, two 6000A solvent delivery pumps, and a 710B sampling processor. The solvent flowed at 2.5 mL per minute through a (C8 cartridge, 10 µm packing and 8 mm diameter by 10 cm long) set in a radial compression Z module. The separations were performed with 100% water. Nitroguanidine had a retention time of 6.5 minutes and nitrosoguanidine around 5 minutes. Injection volumes were 25 µl or 200 µl, run times were 8 or 10 minutes and the detection limits were around 100 µg/Liter. Figure 1 illustrates the separation of these two compounds.

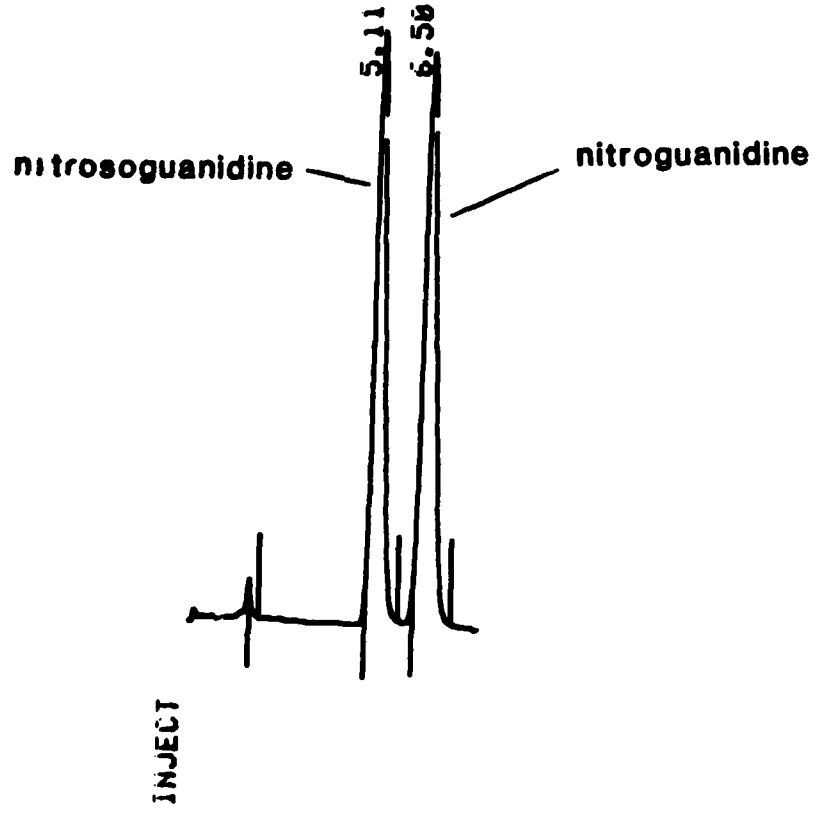


Figure 1. Chromatographic separation of nitroguanidine and nitrosoguanidine.

Nitrates and nitrites were separated and quantified by HPLC. The solvent system consisted of 2.5 mM phosphate buffer flowing at 3 mL per minute through an anion exchange column (SAX 10 um packing, 8 mm diameter by 10 cm long, radial compression cartridge, Waters Associates). The anions were monitored at 229 nm. The retention times were approximately 6 minutes and 5 minutes for nitrate and nitrite, respectively. Injection volumes were 25 µL or 200 µL.

Toxicity to Soil Microorganisms. Soil organisms were grown on both nutrient agar (Difco, Detroit, MI) and soil extract agar. Soil extract agar consisted of one liter of soil extract supplemented with 0.25 g K_2HPO_4, 0.2 g KH_2PO_4, 5.0 g yeast extract (Difco) and 20 g granular agar (Difco). The overlay agar consisted of 60 g/L of granular agar. The inoculated soils were incubated in 50 mL capacity Oak Ridge polypropylene centrifuge tubes, 15 g of soil per tube, at 30°C with varying 50 concentrations of nitroguanidine. After incubation, soils were extracted with 10 mL of 0.85% KCl, vortexed, and 1 mL of the extract was added to 99 mL of sterile distilled water. From this dilution, 0.1 mL was added to the overlay agar and spread on each of the two growth media, incubated at 30°C, and colony forming units (CFU) counted after one and two days of growth.

Batch Soil Studies. Batch soil studies were set up with 15 g dry weight of soil in Oak Ridge polypropylene tubes, 50 mL capacity. Environmental variables including percent organic matter, time, moisture and concentration of nitroguanidine were studied. After incubation, 20 mL of a water/methanol (50/50) solution was added and the tubes were vortexed and then centrifuged. This procedure was repeated twice more, after which the three solutions were filtered through Millex-SR 0.5 µm filters and analyzed separately by HPLC and TLC.

It was found that the methanol/water mixture provided for maximal recovery of nitroguanidine. It was also determined that heating this solution did not improve extraction efficiency. Percent recovery of nitroguanidine was found to be directly dependent on the percent organic matter present in the soil; as the organic content increases, percent recovery decreases.

Guanidine Nitrate. The biodegradability of guanidine nitrate was determined in continuous cultures with BioFlo Model C30 bench top fermenters (New Brunswick Scientific, New Brunswick, NJ). Culture vessels were 500 mL, a mixed inoculum as described earlier was used, and both aerobic and microaerophilic systems were studied. The media contained the following ingredients per liter of tap water: K_2HPO_4, 0.75 g; KH_2PO_4, 1.25 g; $MgSO_4 \cdot 7H_2O$, 0.2 g; $CaCl_2$, 10 mg; NaCl, 10 mg; yeast extract, 0.1 g. Guanidine nitrate, 200 mg/L, and varying amounts of glucose and sucrose were also included. Guanidine nitrate, nitrates, nitrites, ammonia, TOC, pH, and redox potential were determined weekly or twice weekly. Guanidine nitrate was determined by TLC using Eastman cellulose plastic backed plates, in a solvent system of butanol/ethyl acetate/water (4/1/1). The R_f value for guanidine nitrate was around 0.30.

Bioassays. Bioassay work on the nitroguanidine influents and leachates from the soil columns, and the soils from these columns, was performed by the

US Army Environmental Hygiene Agency under the direction of Henry Eichorn. Daphnia and algal tests were run according to standard procedures.[3,4] However, due to repeated delays at USAEHA, no data was available at the time of publication of this report. Data will be made available at a later date through the contracting office, US Army Toxic and Hazardous Materials Agency (USATHAMA).

RESULTS

The continuous flow soil columns were studied over 290 days. For the control tap water column, Figure 2, the levels of nitrate, nitrite, and ammonia were not significant during the course of the study. In addition, no compounds were identified in the soil leachates or tap water which would have interfered with accurate determinations of nitroguanidine, nitrosoguanidine, nitrates, or nitrites.

In Figure 3, the levels of nitrate, nitrite and ammonia are presented for the sterile column, 1.0% mercuric chloride with 150 mg/L nitroguanidine. There was virtually 100% recovery of the nitroguanidine in leachates from this column (Figure 3) and the concentrations of nitrate, nitrite, and ammonia were insignificant (Figure 2).

Figure 4 illustrates the degradation of nitroguanidine, 150 mg/L, in the microbially active column which received varying concentrations of supplemental glucose. Changes in glucose concentration were as follows: no glucose for days 0 through 96; 2.0 g/L for days 97 through 181, 1.0 g/L for days 182 through 243, and 0.5 g/L thereafter. After initiation of this column without glucose, the concentration of nitroguanidine in the effluents from the active and sterile columns steadily increased up to about 25 days, indicating no degradation of nitroguanidine under these conditions. Column breakthrough was within the first week. The degradation of nitroguanidine in the sterile column remained at this level throughout the experiment, indicating little capability of soil physical/chemical interactions towards degrading the nitroguanidine. In the microbially active column, little degradation was in evidence until glucose was added to the feed medium at day 27. Almost immediately, the activity in the column responded so that by about day 115 almost 100% of the nitroguanidine was degraded. This virtually complete degradation continued as long as 2 g/L glucose was present in the feed, as well as when the carbon load was halved to 1.0 g/L at day 182. At day 244, when the carbon load was again halved to 0.5 g/L, there was a resultant decline in degradation efficiency in the column such that by day 290 degradation levels had dropped off to near 25%.

These results indicate that sufficient alternate carbon is required for metabolism of nitroguanidine in soil, as had been previously reported for aqueous systems. The level of carbon required under the conditions of this experiment was between 1.0% and 0.5% glucose, representing a carbon to nitrogen (C/N) ratio of approximately 68 to 1 and 34 to 1, respectively.

Figures 5 through 7 present nitrate, nitrite, and ammonia recovery data corresponding to the degradation results in Figure 4. In Figure 5, ammonia levels in influent feeds and effluent leachates remained below 10 mg/L, until approximately 110 days, at which point the levels increased to around 60 mg/L.

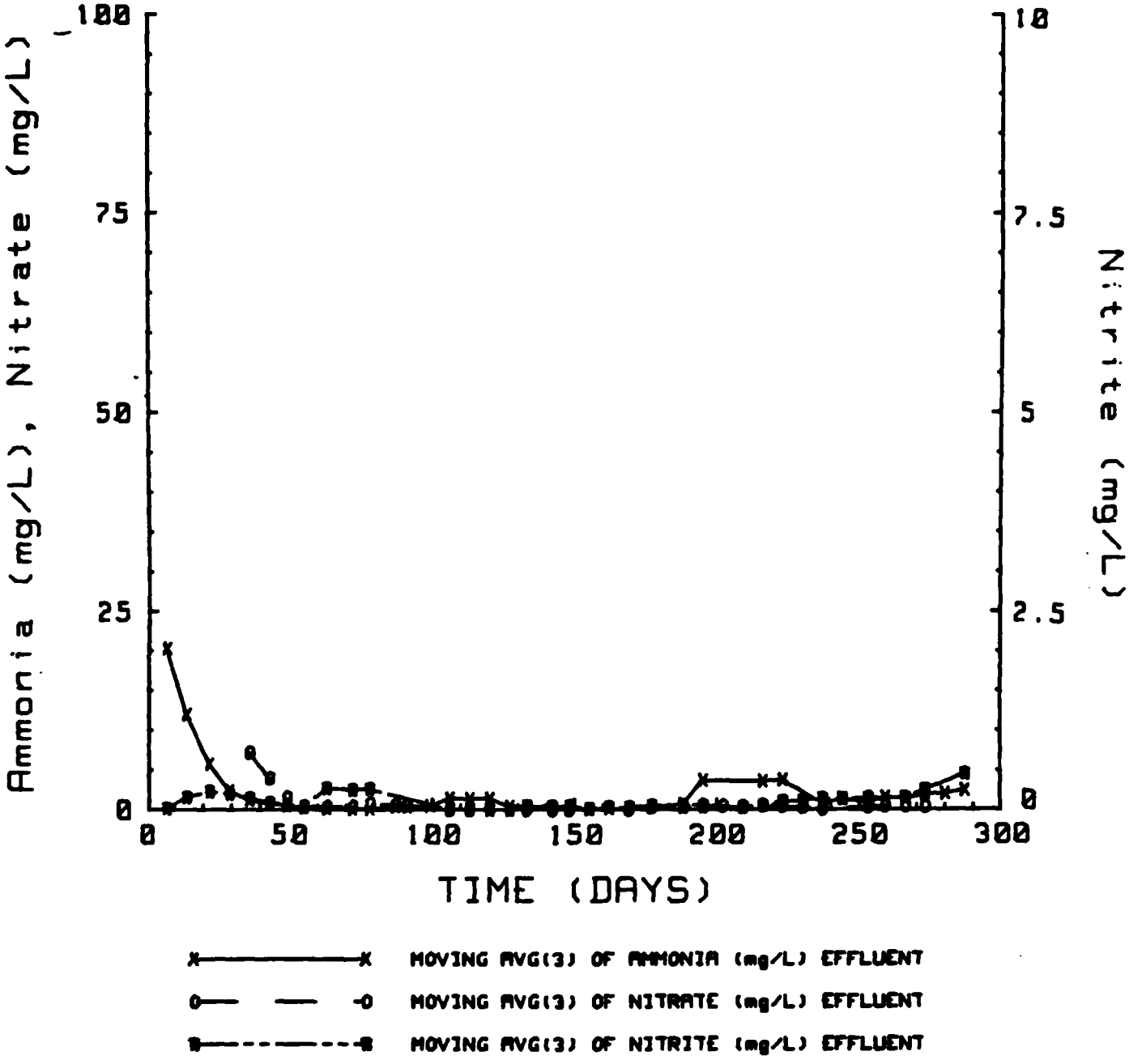


Figure 2. Concentrations of ammonia, nitrate, and nitrite in tap water and soil column leachates from an active control column receiving no nitroguanidine.

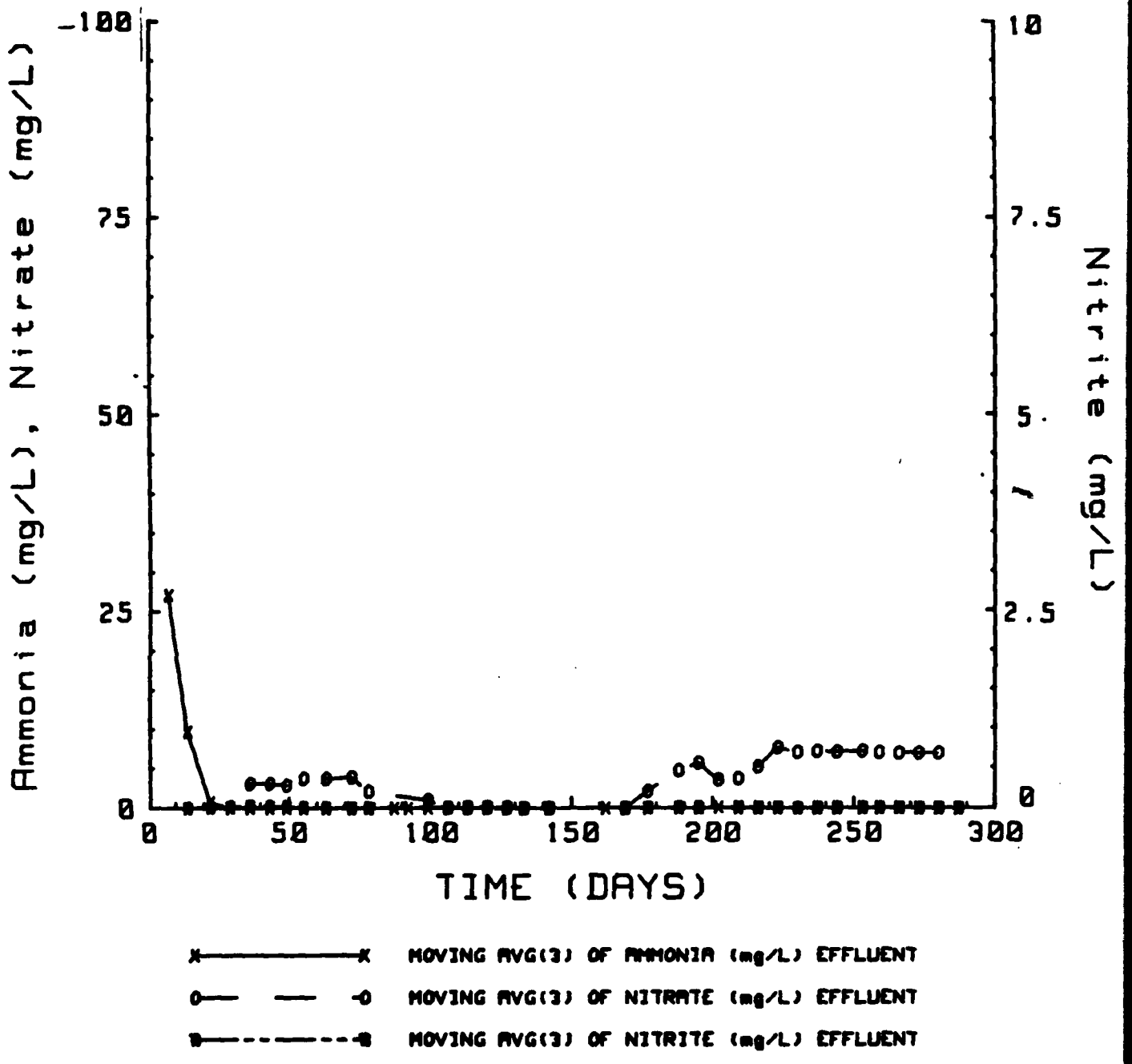


Figure 3. Concentrations of ammonia, nitrate, and nitrite in influent feed and column leachates from the sterile control column receiving 150 mg/L nitroguanidine and 1.0% mercuric chloride.

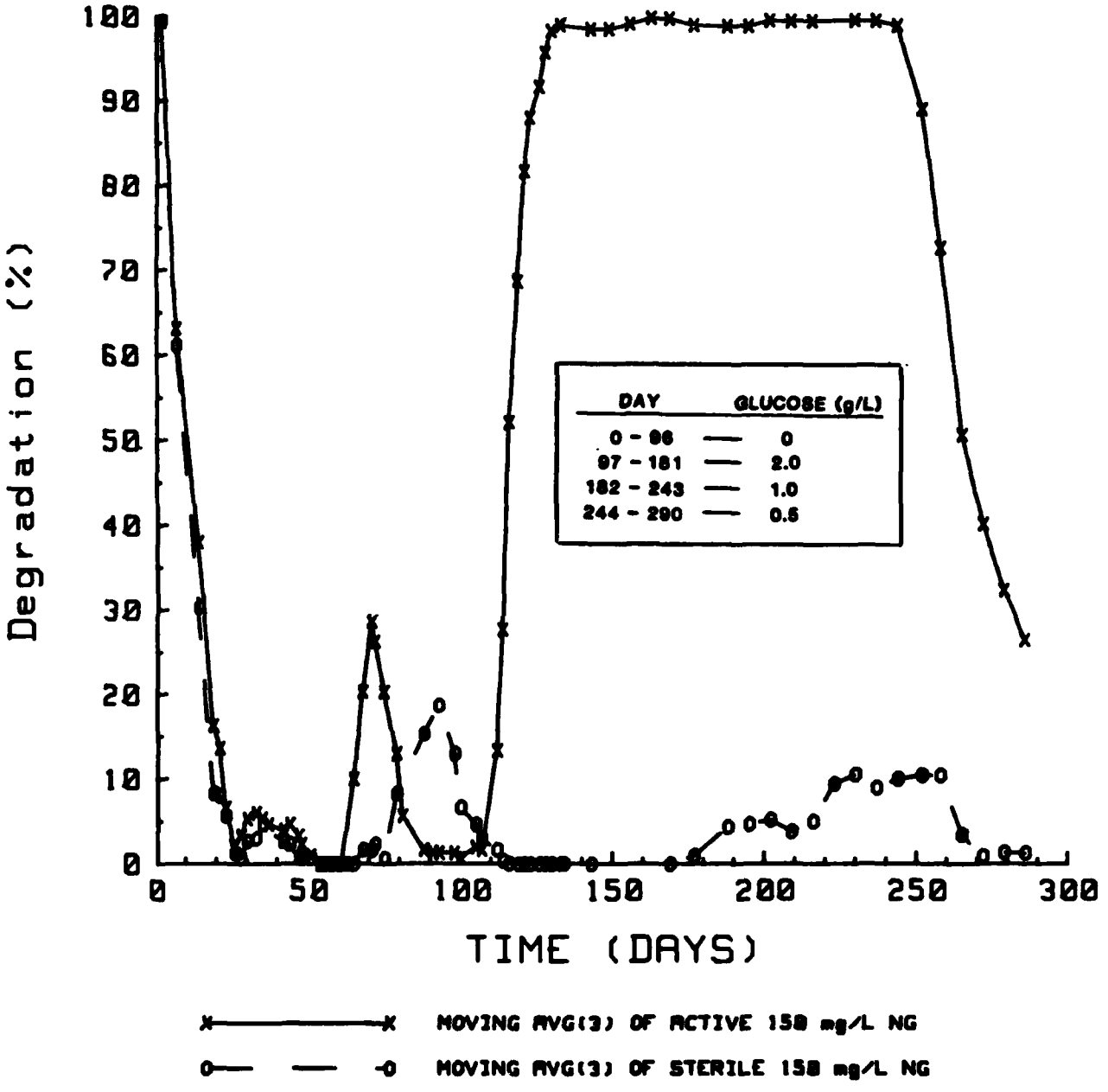


Figure 4. Degradation of nitroguanidine in an active column at varying concentrations of glucose.

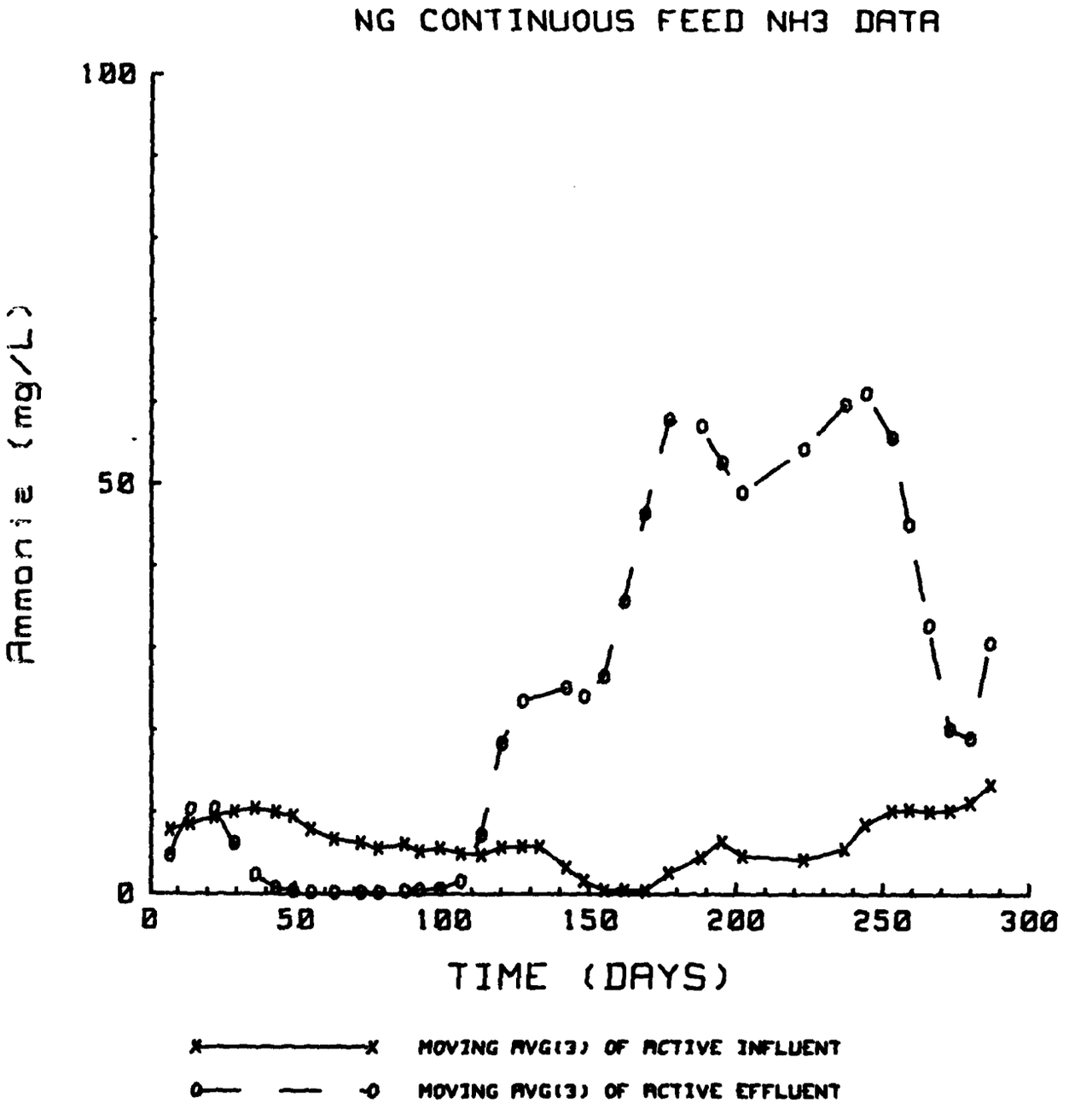


Figure 5. Ammonia recovery data from the active soil column, corresponding to Figure 4.

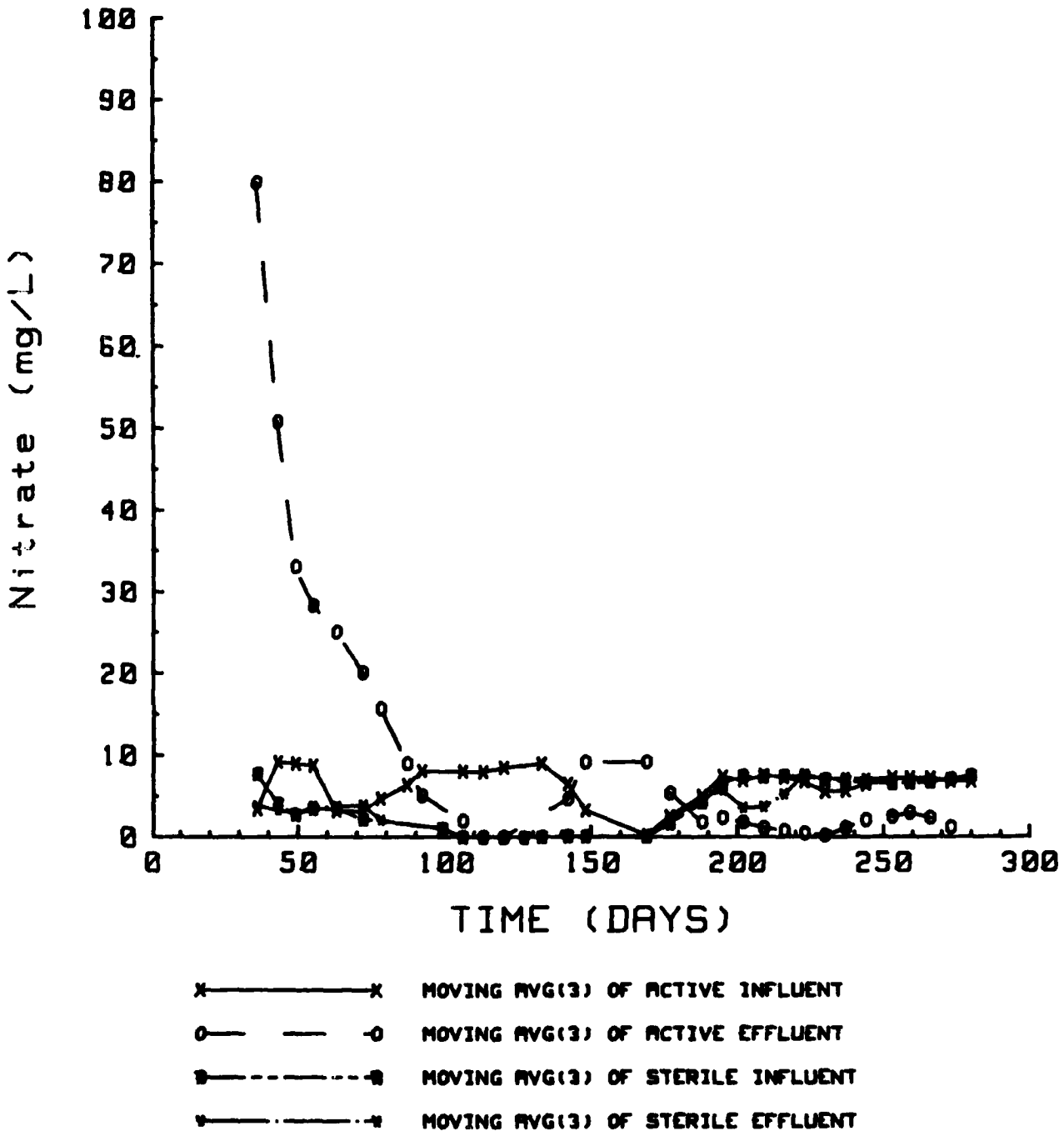


Figure 6. Nitrate recovery data from the active soil column, corresponding to Figure 4.

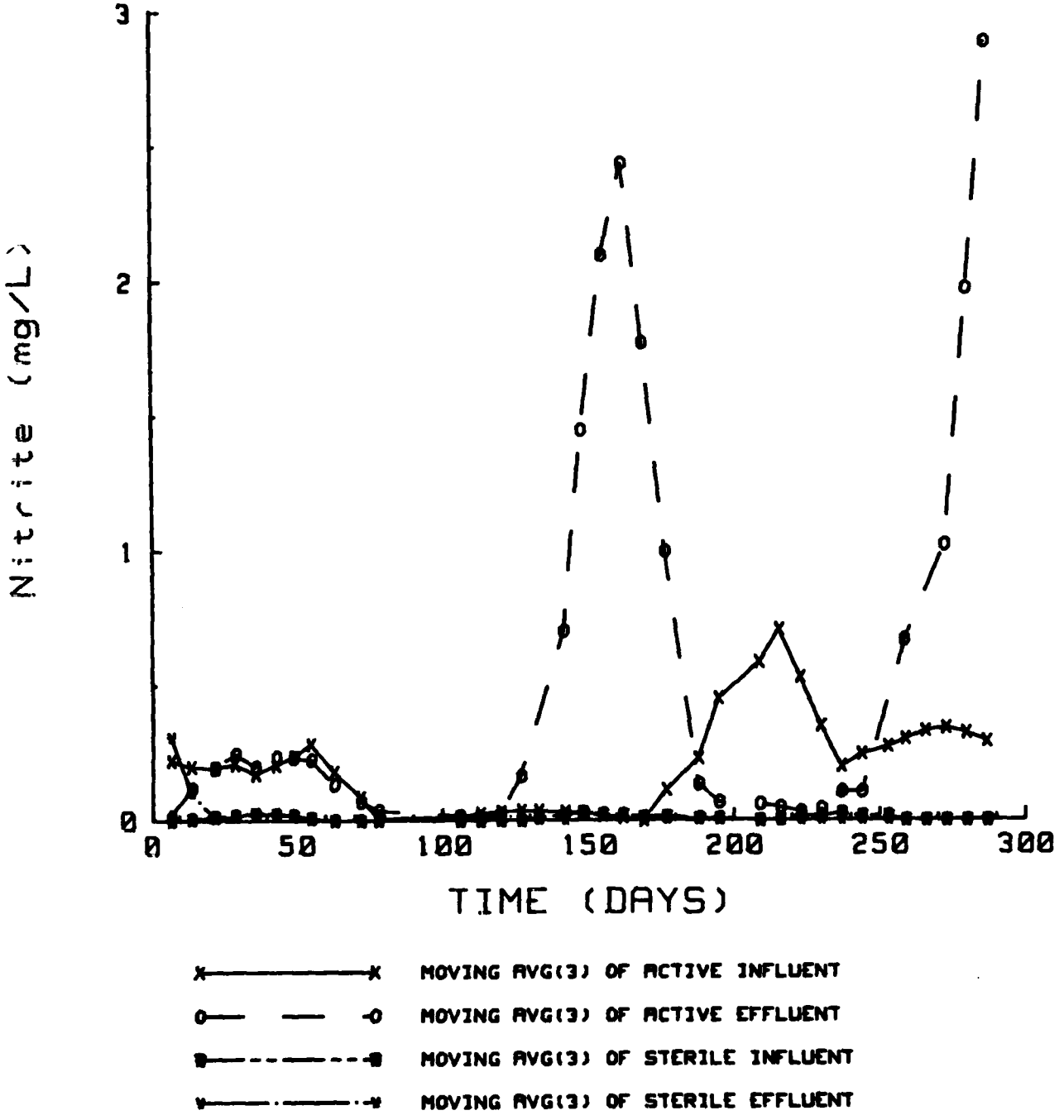


Figure 7. Nitrite recovery data from the active soil column, corresponding to Figure 4.

The rise of ammonia concentration in leachates reflects the corresponding increase in degradation of the nitroguanidine (Figure 4). Also, as the degradation efficiency decreased after the change in glucose concentration to 0.5 mg/L, the ammonia concentration in the leachates also decreased. Throughout the study the levels of ammonia in column leachates reflected the degradation activity towards nitroguanidine. Concentrations of ammonia in column influents remained low, throughout the study.

Similar data for nitrate is presented in Figure 6. Aside from an initial high level which drops off successively with time, no significant nitrate levels were present in column leachates. Similar results were found with nitrite concentrations, although periodic fluctuations were noted up to around 3 mg/L (Figure 7). We do not feel this fluctuation is a concern because some fluctuations were also noted in influent concentrations, and for the most part nitrite concentrations remained in the µg/L (ppb) range. During the period of optimum degradation of nitroguanidine, nitrite levels were not continuously in the mg/L range.

The data from Figures 5 through 7 are combined into one illustration in Figure 8. Here, the degradation of nitroguanidine and the concurrent rise in ammonia level is evident. Along with this picture is the fact that nitrosoguanidine concentrations measured on a weekly basis did not reach significant levels (<100 µg/L). In addition, 100-fold concentrates of leachates from this column produced no evidence for metabolic intermediates. The nitrosoguanidine present in trace amounts was presumably very unstable in the soil environment and thus did not build up to significant concentrations.

In a separate soil column initiated to evaluate the efficacy of 0.75 g/L glucose as a cometabolite in degrading nitroguanidine, Figure 9, only intermediate levels of degradation were achieved. Thus it is clear that around 1.0 g/L glucose, under the conditions of this study, was required to optimize the degradation of the nitroguanidine.

Results of TOC analysis are illustrated in Table 2. Organic loads were reduced about 70% to 80% with the varous glucose concentrations. The

TABLE 2. TOC Results for Soil Columns

Column No.	Glucose (mg/L)	Influent (mg/L)[b]	Effluent (mg/L)[b]	Decrease (%)[b]
3	0	13.1 ± 5.6 (5)	89.4 ± 22.6 (3)	---[c]
2	0	14.1 ± 5.0 (5)	66.3 ± 21.3 (5)	---
2	0.5	218.2 ± 10.3 (5)	62.5 ± 21.0 (5)	71.7 ± 8.1 (5)
2	1.0	419.4 ± 19.1 (5)	106.7 ± 15.4 (5)	74.5 ± 3.8 (5)
2	2.0	811.4 ± 36.7 (5)	115.0 ± 52.3 (5)	79.8 ± 10.7 (4)
4	0.75	308.8 ± 11.9 (4)	95.2 ± 47.7 (4)	69.5 ± 14.0 (4)

[a]reference Table 1 for column conditions.
[b]average ± 1 standard deviation; number of samples in parentheses.
[c]no decrease.

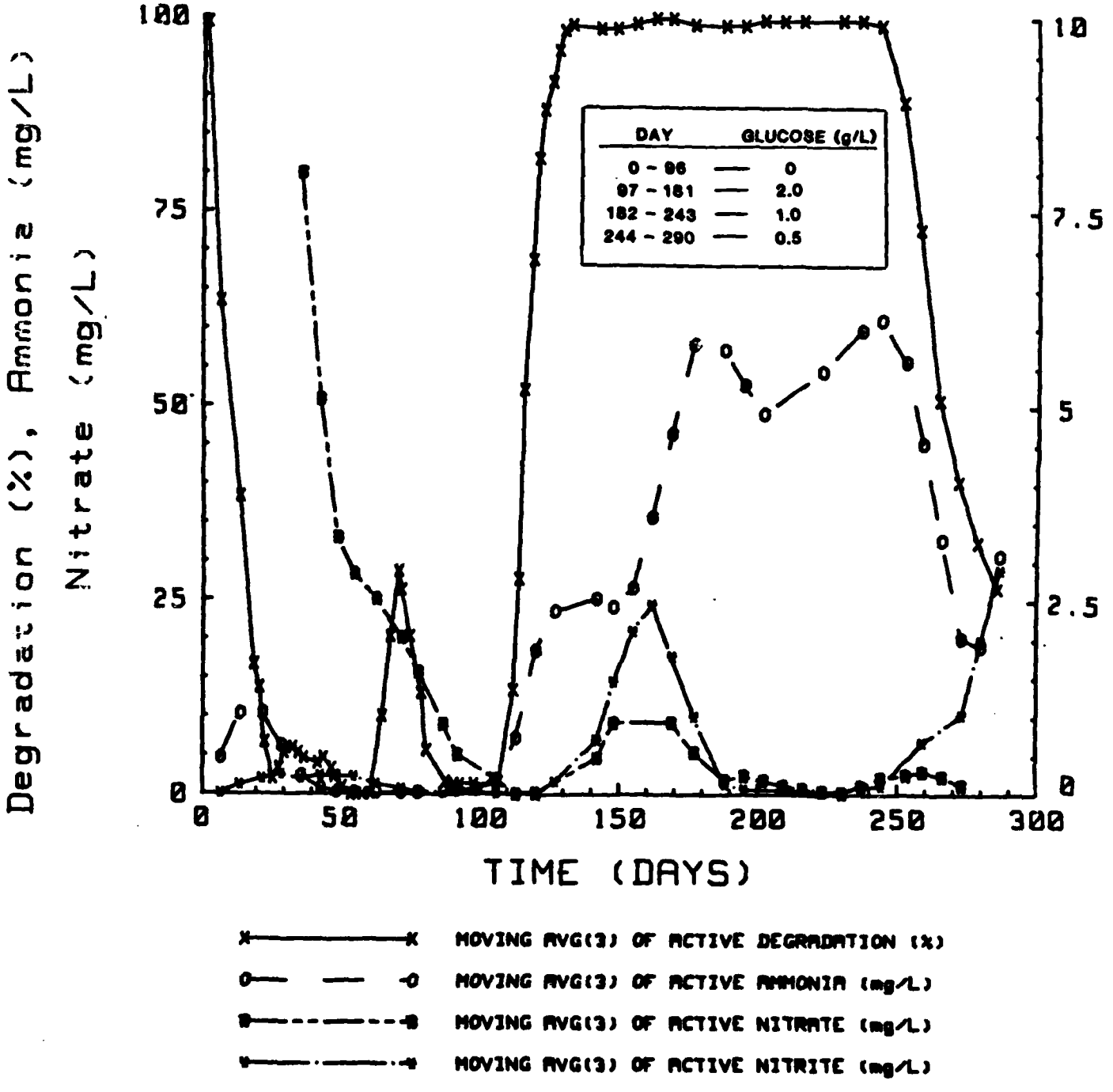


Figure 8. Combined data from the active soil column receiving 150 mg/L nitroguanidine.

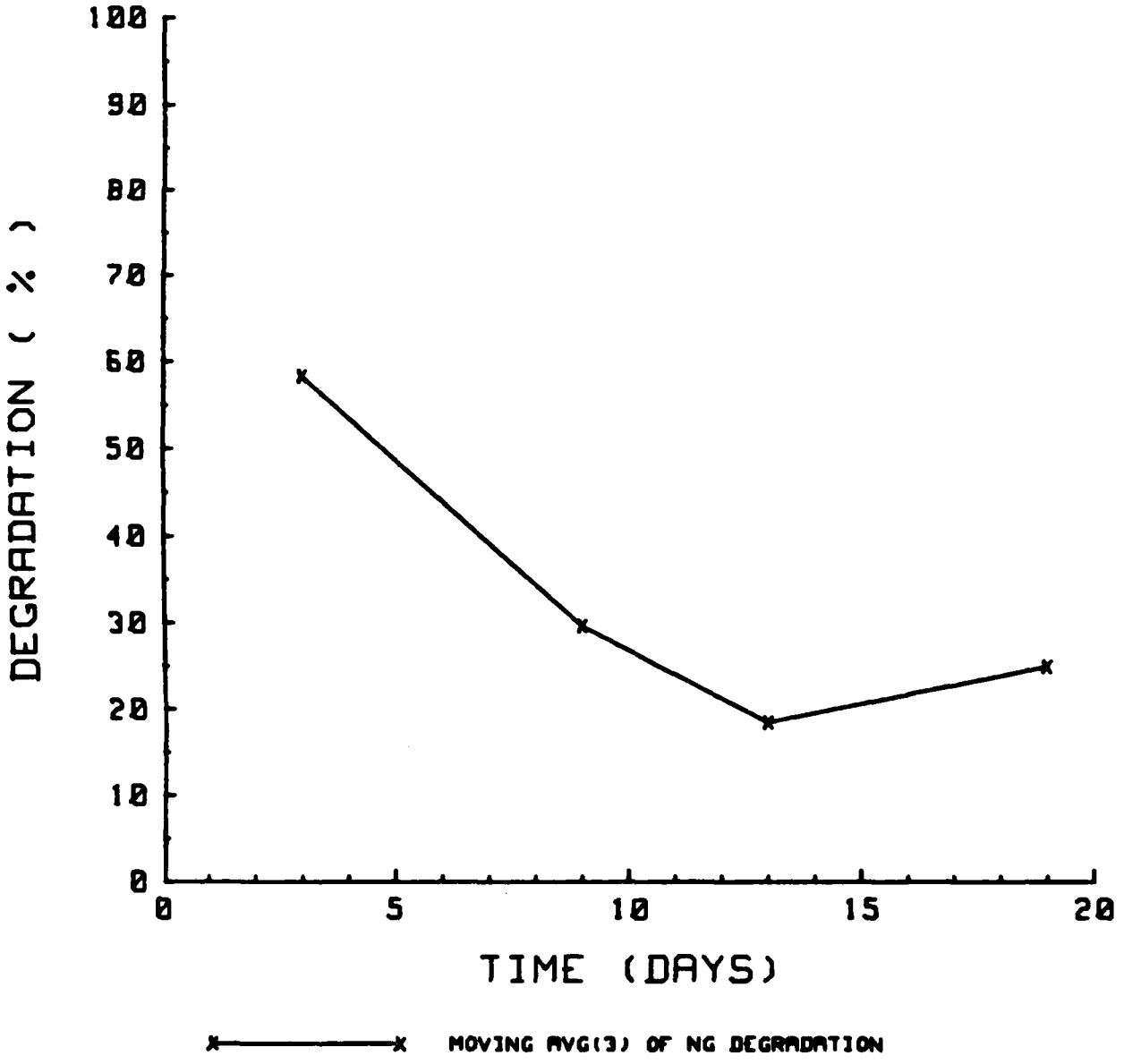


Figure 9. Degradation of nitroguanidine in an active soil column with 0.75 g/L glucose.

remaining organic load is not primarily due to the glucose loadings but due to organic leachates from the soil itself; note the effluent concentrations when no glucose was present in the influent. It appears that carbon additions necessary for the cometabolism of nitroguanidine should have a minimal impact on groundwater in terms of additional carbon load, provided proper controls are used and the system is monitored.

Results from tests of toxicity of nitroguanidine on soil microorganisms are illustrated in Figure 10. There was no apparent toxicity at nitroguanidine concentrations from 0.01 ug/g soil up to 10 mg/g soil (1%) after 48 hours of incubation.

DISCUSSION

The results from continuous flow laboratory scale soil column studies indicated that short-term land treatment would be a viable option, provided proper application controls are followed. Sufficient alternate carbon would have to be provided in order to insure the degradation of the nitroguanidine. In addition, the fine-tuning of this carbon requirement would be dependent on the concentration of nitroguanidine in the wastewater, the flow rates and hydraulic loading of the soil, soil type, the presence of other organics and inorganics, and other environmental factors. Thus, it would be essential to adequately monitor process waters, groundwaters, and the soil to assure that proper application process controls are in effect. Significant problems would ensue if appropriate carbon loads were not used. With insufficient carbon supplementation it would be expected that the nitroguanidine applied to the soil would leach directly into groundwater due to the solubility in water and lack of cometabolic energy. Additional carbon, as cometabolic energy, would be essential for the biodegradation process.[2] In addition, a variety of commercially available carbon sources could be evaluated for this application.[5]

It was also important to note that during the degradation of nitroguanidine in continuous flow soil columns, no significant concentrations of potentially hazardous organic intermediates were detected. Nitrosoguanidine, a nitrosamine which has been identified at significant concentrations in aqueous systems, did not appear at significant concentrations in the leachates from the soil columns, nor did the other organic-nitrogen intermediates previously identified. During the degradation of nitroguanidine, nitrates and nitrites remained at background levels, while ammonia concentrations rose significantly. Ammonia is the primary end-product of this degradation.

At loading rates of approximately 110 mg/L of nitroguanidine on average in the feed solution during optimal degradation activity, a maximum of around 60 mg/L of ammonia was produced in the leachates. In terms of mass balance, the nitrogen contained in this quantity of ammonia accounts for around 85% of

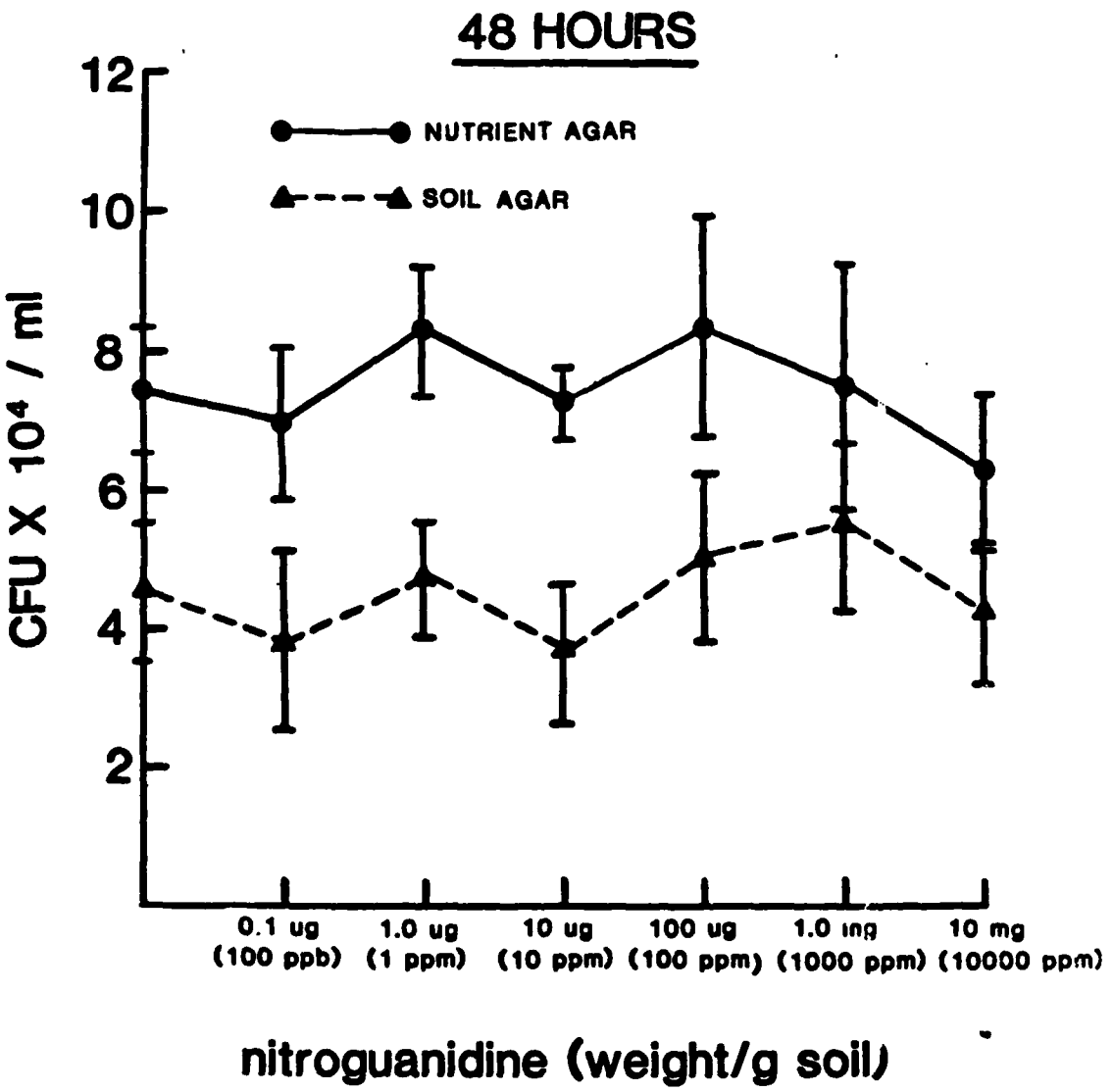


Figure 10. Absence of toxicity of nitroguanidine to soil microorganisms over a range of concentrations.

the nitrogen in the nitroguanidine feed. Presumably the remaining 15% could be accounted for by some volatilization of ammonia, formation of trace levels of nitrates or nitrites, and incorporation into organic-nitrogen compounds for microbial biomass.

For short-term land application systems, monitoring requirements would have to include, at the minimum, analysis for nitrosoguanidine, nitroguanidine, nitrates, nitrites, ammonia, total organic carbon and total nitrogen in process waters, groundwater and soils.

Extrapolations for land application rates could be made based on the surface area (44.2 cm^2) of the soil columns studied, the feed rates, approximately 100 mL/day, and the amount of nitroguanidine, approximately 10 mg/day. Extrapolations to acreage would give an equivalent of about 22,700 gallons/day or 86,000 liters/day per acre, containing 9.1 kg or 20 pounds of nitroguanidine/day per acre.

Long-term applications of nitroguanidine-laden wastewaters to soils are not recommended due to insufficient study periods upon which to extrapolate to longer exposures, and limitations due to inorganic and organic nutrient loading of the soil.

As an alternative cost-effective, long-term solution, a wastewater treatment system design could be developed which would rely mainly on biological approaches for treatment of wastewater; however, this would also require some physical or chemical processes to supplement the basic biological approach. The biodegradation of nitroguanidine has previously been demonstrated to be an anaerobic or microaerophilic process, and this should be a primary design criterion. In addition, air stripping for the ammonia produced could be considered. Final treatment of process waters could be accomplished with land application, having already reduced nutrient loading and the concentration of the hazardous compounds. Another point for consideration is the significantly greater C/N ratio required for the complete degradation of nitroguanidine in soil as compared to aqueous systems. Considerable cost savings in the alternate carbon requirements would therefore be realized by using an aqueous treatment system as opposed to a land-based system.

Guanidine nitrate, the precursor to nitroguanidine during nitroguanidine manufacture, will also be present in process waters. Preliminary biodegradation studies were performed and guanidine nitrate was found to be biodegradable, primarily under anaerobic or microaerophilic conditions.

An extensive literature search was performed through Natick's resources as well as those of the Hazardous Materials Technical Center, Rockville, MD. Data bases searched included Chemline, TBD, CHMTADS, RTECS, Hazardline, NITS, Toxline, Medline, Biosis, Embase, Chemical Exposure, Life Sciences Collection, Sci Search, CA Search, Arthur Little Online, Agricola, Conference Papers

Index, Enviroline, Environmental Bibliography, Pollution Abstracts, Federal Research Progress, Compendex, and EI Engineering Meetings. The key words used in the search were the following: guanidine nitrate, CAS #506-93-4, metabolism, stability, biodegrade, degrad, persistence, fate, toxic, hazard, health, injurious. Little information turned up this search; however, in one report it was found that guanyl compounds, including guanidine, cyanoguanidine and guanylurea degraded under anaerobic conditions but not in activated (aerobic) sludge.[6] From this report, our preliminary findings, and based on the structure of guanidine nitrate, it would appear that guanidine nitrate will biodegrade under similar conditions as nitroguanidine; that is, anaerobic conditions with a supplemental carbon requirement.

CONCLUSIONS

Nitroguanidine could be treated with a short-term land application system provided sufficient supplemental carbon is provided for cometabolic needs. Ammonia is the primary product formed during the degradation of nitroguanidine in soil. Only trace levels of nitrosoguanidine were detected, while insignificant levels of other organic-nitrogen compounds were present in leachates from the soil columns. Nitrate and nitrite levels also remained near background. The ammonia produced during the degradation of nitroguanidine accounts for approximately 85% of the total applied nitrogen.

Without sufficient supplemental carbon, the nitroguanidine will not degrade and will leach into groundwaters. Preliminary work with guanidine nitrate indicated that this compound was biodegradable and this process will require supplemental carbon as well.

Recommendations for monitoring requirements for a land application system are provided as well as a general concept for a processing plant for longterm treatment of nitroguanidine-laden wastewaters.

This document reports research undertaken at the US Army Natick Research and Development Command and has been assigned No. NATICK/TR-85/047 in the series of reports approved for publication.

LITERATURE CITED

1. Kistner, S. L. , M. D. Nickelson and J. J. Resta. Phase I Land treatment feasibility study No. 32-24-0410-83, Sunflower AAP, DeSoto Kansas, 6-10 Dec 1982. US Army Environmental Hygiene Agency, Aberdeen Proving Ground, MD 21010 (1983).

2. Kaplan, D. L., J. H. Cornell and A. M. Kaplan. Decomposition of nitroguanidine. Env. Sci. Technol. 16(8):488-492 (1982).

3. Christensen, E. R. and N. Nyholm. Ecotoxicological assays with algae: Weibull dose-response curves. Env. Sci. Technol. 18:713-718 (1984).

4. Standard Methods for the Examination of Water and Wastewater. Bioassay Procedures for Daphnia 804B. Public Health Assoc. American Water Works Assoc. and Water Poll. Control Federation. pp. 663-666 (1980).

5. Kaplan, D. L., P.A. Riley, J. Pierce and A. M. Kaplan. Denitrification-efficiencies of alternate carbon sources. NATICK/TR-85/003. US Army Natick R&D Center, Natick, MA 01760-5020 (1985). (AD A148 029)

6. Ebisuno, T. and M. Takimoto. Examination of the biodegradability of guanyl compounds. Eisei Kagaku 27(3):156-162 (1981).